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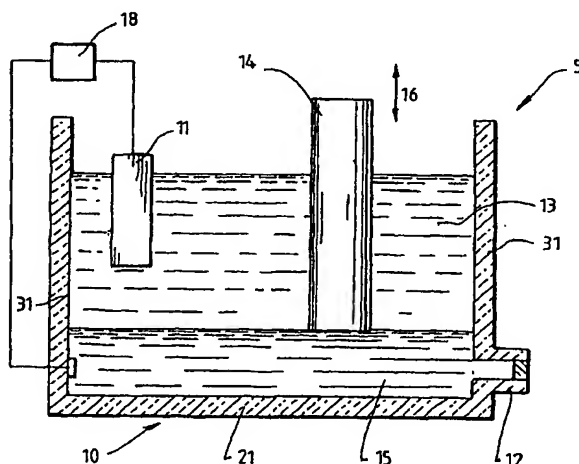
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(54) Title: ELECTROLYTIC REDUCTION OF METAL OXIDES



(57) Abstract: A method of electrolytically reducing a metal oxide (such as aluminium and magnesium oxides) to produce a metal in an electrolytic cell is disclosed. The method includes electrolytically reducing the metal oxide in an electrolytic cell that includes a pool of molten metal, the metal being the metal of the metal oxide to be reduced, and the molten metal pool forming a cathode of the cell. The electrolytic cell also includes a pool of molten electrolyte in contact with the molten metal, the electrolyte containing alkali and/or alkaline earth halides. The electrolytic cell also includes an anode extending into the electrolyte and a body of metal oxide to be reduced in contact with the molten metal and the electrolyte.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

ELECTROLYTIC REDUCTION OF METAL OXIDES

1. Field of the Invention

5 The present invention relates to electrolytic reduction of metal oxides to produce substantially pure metals.

10 In particular, the present invention relates to electrolytic reduction of aluminium and magnesium oxides using a CaCl_2 electrolyte.

2. Background Art

15 The present invention was made during the course of an on-going research project on the electrolytic reduction of metal oxides using CaCl_2 -based electrolyte being carried out by the applicant.

20 The research project investigated electrolytic reduction of a range of metal oxides in electrolyte cells based on the use of using CaCl_2 electrolyte.

25 The CaCl_2 electrolyte was a commercially available source of CaCl_2 , namely calcium chloride dihydrate, that decomposed on heating and produced a very small amount of CaO .

30 The applicant operated the electrolytic cells at a potential above the decomposition potential of CaO and below the decomposition potential of CaCl_2 .

35 The applicant found that the cells could electrolytically reduce a range of metal oxides to metals with very low concentrations of oxygen.

3. Summary of the Invention

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The present invention provides, in broad terms, a method of electrolytically reducing a metal oxide to produce a metal in an electrolytic cell, which method includes electrolytically reducing the metal oxide in an electrolytic cell that includes (a) a pool of molten metal, the metal being the metal of the metal oxide to be reduced, the molten metal pool forming a cathode of the cell, (b) a pool of molten electrolyte in contact with the molten metal, the electrolyte containing alkali and/or alkaline earth halides, (c) an anode extending into the electrolyte, and (d) a body of metal oxide to be reduced in contact with the molten metal and the electrolyte.

In the above method electrolytic reduction of metal oxide takes place where there is contact between (i) the molten metal, (ii) the metal oxide, and (iii) the electrolyte.

Preferably the metal oxide body has a geometric shape that maximises contact between (i) the molten metal, (ii) the metal oxide, and (iii) the electrolyte..

Preferably the method includes feeding the metal oxide body into the electrolytic cell to maintain contact of the metal oxide and the molten metal.

The metal oxide body may be in many forms, including rods, plates, blocks and the like, which can be readily immersed into the electrolyte and brought into contact with the molten metal.

Preferably the method includes maintaining the cell temperature above the melting points of the electrolyte and the metal of the metal oxide to be reduced.

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Preferably the method includes operating the cell at a potential that is above a decomposition potential of at least one constituent of the electrolyte so that there are cations of a metal other than that of the cathode metal oxide in the electrolyte.

Preferably the metal oxide is an aluminium oxide or a magnesium oxide.

In a situation in which the metal oxide is a aluminium oxide or magnesium oxide it is preferred that the electrolyte be a CaCl_2 -based electrolyte that includes CaO as one of the constituents.

In such a situation it is preferred that the cell potential be above the decomposition potential for CaO .

It is also preferred that the cell potential be below the decomposition potential for CaCl_2 .

It is preferred that the cell potential be less than 3.0V.

It is preferred particularly that the cell potential be below 2.5V.

It is preferred more particularly that the cell potential be below 2.0V.

It is preferred that the cell potential be at least 1.5V.

The CaCl_2 -based electrolyte may be a commercially available source of CaCl_2 , such as calcium chloride dihydrate, that partially decomposes on heating and produces CaO or otherwise includes CaO .

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Alternatively, or in addition, the CaCl_2 -based electrolyte may include CaCl_2 and CaO that are added separately or pre-mixed to form the electrolyte.

5 At this stage, the applicant does not have a clear understanding of the electrolytic cell mechanism when the cell is operated at a potential at which CaCl_2 -based electrolyte partially decomposes. Nevertheless, whilst not wishing to be bound by the comments in this
10 paragraph, the applicant offers the following comments by way of an outline of a possible cell mechanism. The applicant believes that operating the electrolytic cell above a potential at which CaCl_2 -based electrolyte partially decomposes produces Ca^{++} cations that migrate to
15 the vicinity of the metal oxide in contact with the molten metal cathode and provide a driving force that facilitates extraction of O^{--} anions produced by electrolytic reduction to metal of metal oxide in contact with the molten metal cathode. The applicant also believes that the O^{--} anions,
20 once extracted from the metal oxide, migrate to the anode and react with anode carbon and produce CO and release electrons that facilitate electrolytic reduction of metal oxide to metal. The experimental work carried out by the applicant produced evidence of Ca metal in the
25 electrolyte. The applicant believes that the Ca metal was the result of electrodeposition of Ca^{++} cations as Ca metal on electrically conductive sections of the cathode and that at least part of the Ca metal dissolved in the electrolyte and migrated to the vicinity of the metal
30 oxide in the cathode and participated in chemical reduction of oxides.

It is preferred that the anode be graphite.

35 Preferably the cell includes a base and side walls extending upwardly from the base formed from graphite.

Preferably the cell includes at least one tap hole for molten metal in one of the side walls and the method includes removing molten metal continuously or periodically.

The above-described method may be started-up in a number of ways.

One option is to introduce the (pure) metal and the electrolyte in solid state into the cell and subsequently heat the entire system to melt the metal and the electrolyte.

Another option is to introduce molten metal and molten electrolyte separately into the cell.

The following example illustrates an application of the invention in the process of reducing aluminium oxide (alumina) into substantially pure aluminium using an electrolytic cell as illustrated in Figure 1.

4. Description of Exemplary Embodiment

Figure 1 is a schematic illustration of an electrolytic cell 5 that can be scaled-up in application of the present invention.

Whilst the example described below relates to the reduction of alumina, the basic principle is equally applicable to other metals, particularly low melting point metals, more particularly magnesium.

The electrolytic cell 5 of Figure 1 includes a graphite crucible 10 that has a base 21, side walls 31, and a tapping/discharge opening indicated as 12 in one of the side walls 31.

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The electrolytic cell 5 further includes a bath of molten CaCl_2 electrolyte 13 in the crucible and a graphite electrode 11 immersed in the molten electrolyte 13. The graphite electrode 11 forms the anode of the cell 5.

The electrolytic cell 5 further includes a pool 15 of molten aluminium in a lower section of the crucible 10. The molten aluminium pool 15 forms the cathode of the cell.

The electrolytic cell further includes a body 14 that consists of or incorporates alumina (Al_2O_3) to be reduced and extends into the electrolyte 13 and contacts the molten aluminium cathode 15. The alumina is shaped as a rod, sheet or prismatic body. Alumina body 14 is held in an appropriate manner to allow controlled movement into and away from the crucible interior as indicated by the arrow 16.

The electrolytic cell 5 further includes a suitable power source 18 connected to the anode 11 and to the molten aluminium cathode 15.

The molten aluminium cathode 15 is required in order to initiate electrolytic reduction of the alumina in the alumina body 14 to aluminium. The electrolytic reduction process is carried out at an elevated temperature of around 950°C at which the CaCl_2 electrolyte is and remains molten. On immersion of the alumina body 14 into the electrolyte 13 and subsequent contact of the alumina body 14 with the molten aluminium cathode 15, reduction of the alumina takes place. Since the process temperatures are above the melting point of aluminium, the latter will melt into the bath 15 and the bath level within crucible 10 will tend to rise.

In order to maintain optimum reduction conditions, the alumina body 14 is moved at a rate commensurate with the melting-off rate of aluminium from the alumina body 14 and the build-up of aluminium so that immersion of the alumina body 14 in the molten aluminium is kept at a minimum.

The process may be operated in a continuous mode by removing molten aluminium through tap hole 12 and positioning additional alumina bodies 14 in the electrolyte 13 to replace bodies 14 that are consumed in the reduction process.

Many modifications may be made to the embodiment of the present invention described above without departing from the spirit and scope of the present invention.

CLAIMS:

5

1. A method of electrolytically reducing a metal oxide to produce a metal in an electrolytic cell, which method includes electrolytically reducing the metal oxide in an electrolytic cell that includes a pool of molten metal, the metal being the metal of the metal oxide to be reduced, the molten metal pool forming a cathode of the cell, a pool of molten electrolyte in contact with the molten metal, the electrolyte containing alkali and/or alkaline earth halides, an anode extending into the electrolyte, and a body of metal oxide to be reduced in contact with the molten metal and the electrolyte.

2. The method defined in claim 1 wherein the metal oxide body has a geometric shape that maximises contact between (i) the molten metal, (ii) the metal oxide, and (iii) the electrolyte.

3. The method defined in claim 1 or claim 2 includes feeding the metal oxide body into the electrolytic cell to maintain contact of the metal oxide and the molten metal.

4. The method defined in any one of the preceding claims wherein the metal oxide body includes rods, plates and blocks that can be readily immersed into the electrolyte and brought into contact with the molten metal.

5. The method defined in any one of the preceding claims includes maintaining the cell temperature above the melting points of the electrolyte and the metal of the metal oxide to be reduced.

6. The method defined in any one of the preceding claims includes operating the cell at a potential that is above a decomposition potential of at least one
5 constituent of the electrolyte so that there are cations of a metal other than that of the cathode metal oxide in the electrolyte.
7. The method defined in any one of the preceding
10 claims wherein the metal oxide is an aluminium oxide or a magnesium oxide.
8. The method defined in claim 7 wherein the
15 electrolyte is a CaCl_2 -based electrolyte that includes CaO as one of the constituents.
9. The method defined in claim 8 includes
maintaining the cell potential above the decomposition
20 potential for CaO .
10. The method defined in claim 8 or claim 9 includes
maintaining the cell potential below the decomposition
potential for CaCl_2 .
- 25 11. The method defined in claim 10 includes
maintaining the cell potential less than 3.0V.
12. The method defined in claim 10 includes
maintaining the cell potential less than 2.5V.
30
13. The method defined in claim 10 includes
maintaining the cell potential less than 2.0V.
14. The method defined in any one of claims 8 to 13
35 includes maintaining the cell potential to be at least
1.5V.

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15. The method defined in any one of the preceding claims wherein the cell includes at least one tap hole for molten metal and the method includes removing molten metal continuously or periodically via the tap hole.

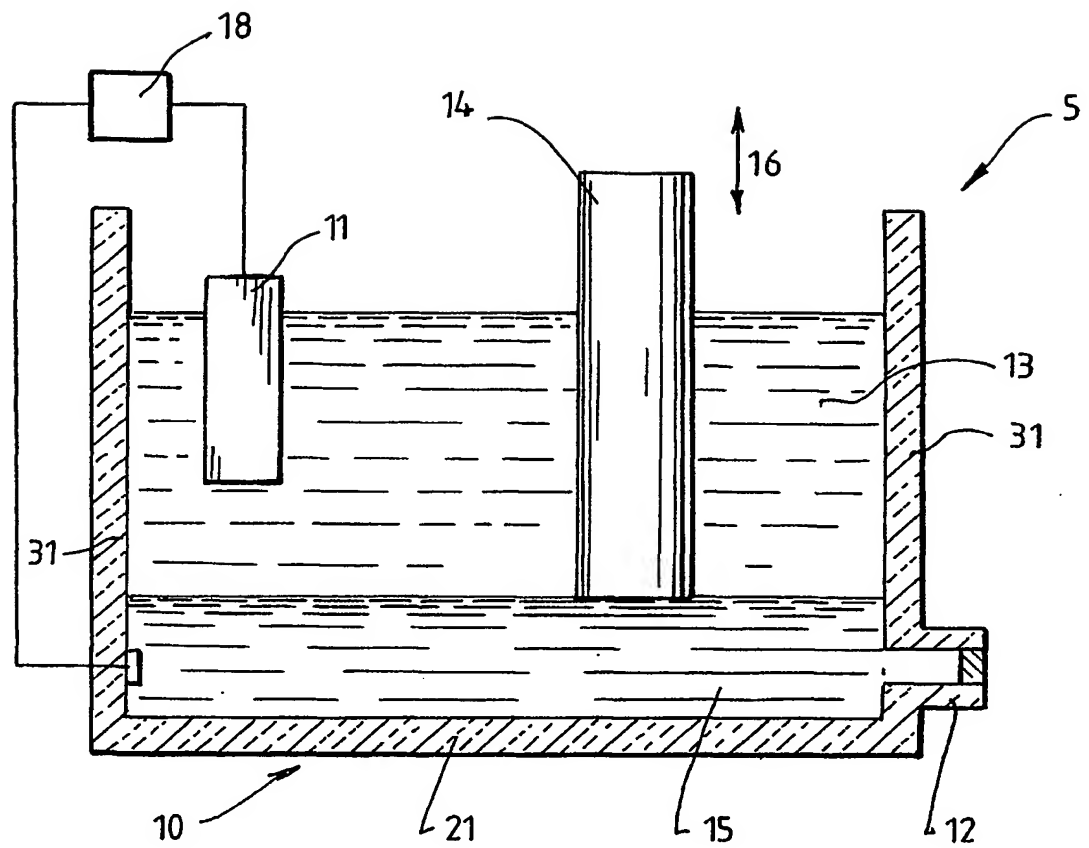


FIG. 1.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTERInt. Cl. ⁷: C25C 3/00, 3/02, 3/04, 3/06, 3/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C25C 3/00, 3/02, 3/04, 3/06, 3/18

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DWPI: HALID+, CHLORID+, FLUORID+, BROMID+, IODID+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5378325 A (DASTOLFO, Jr. et al.) 3 January 1995 col 3, line 51 to col 4, line 9, col 4, line 41 to col 5, line 2, claims 1, 7 and 11 and fig. 2	1-5, 7, 15
X	US 4455202 A (SINTIM-DAMOA et al.) 19 June 1984 col 2, lines 36 to 68, col 3, lines 39-41 and lines 57-68 and claim 1	1-5, 7, 15
X	US 3951763 A (SLEPPY et al.) 20 April 1976 col 2, lines 35-38, claims 1, 5, 11, 15, 16 and fig. 1	1-5, 7, 15

☒ Further documents are listed in the continuation of Box C☒ See patent family annex

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

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INTERNATIONAL SEARCH REPORT

International Application No.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 747509 A (GENERAL MOTORS CORPORATION) 11 December 1996 col 3, line 43 to col 5, line 56, claim 1 and fig. 1	1-5, 7, 15
A	EP 286176 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 12 December 1988 whole document	1-15
A	US 4973390 A (CHRISTINI et al.) 27 November 1990 whole document	1-15

INTERNATIONAL SEARCH REPORT
Information on patent family members

International Application No.
PCT/AU02/00456

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member			
US	5378325	US	5279715	US	5415742
US	4455202	NONE			
US	3951763	BR	7405161	CH	615700
		FR	2235212	IT	1016149
		SE	7406897	YU	1699/74
		US	3855086	US	3852173
EP	747509	AU	52257/96	CA	2176791
		IL	118253	JP	9003682
		US	5593566	CN	1143693
EP	286176	AU	13831/88	DK	1745/88
		JP	63262492	NO	881438
		ZA	8802026	FI	881524
US	4973390	NONE			
					END OF ANNEX